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Liquid Fuel Production by Fast Pyrolysis of Biomass

September 2013. DTU International Energy Conference

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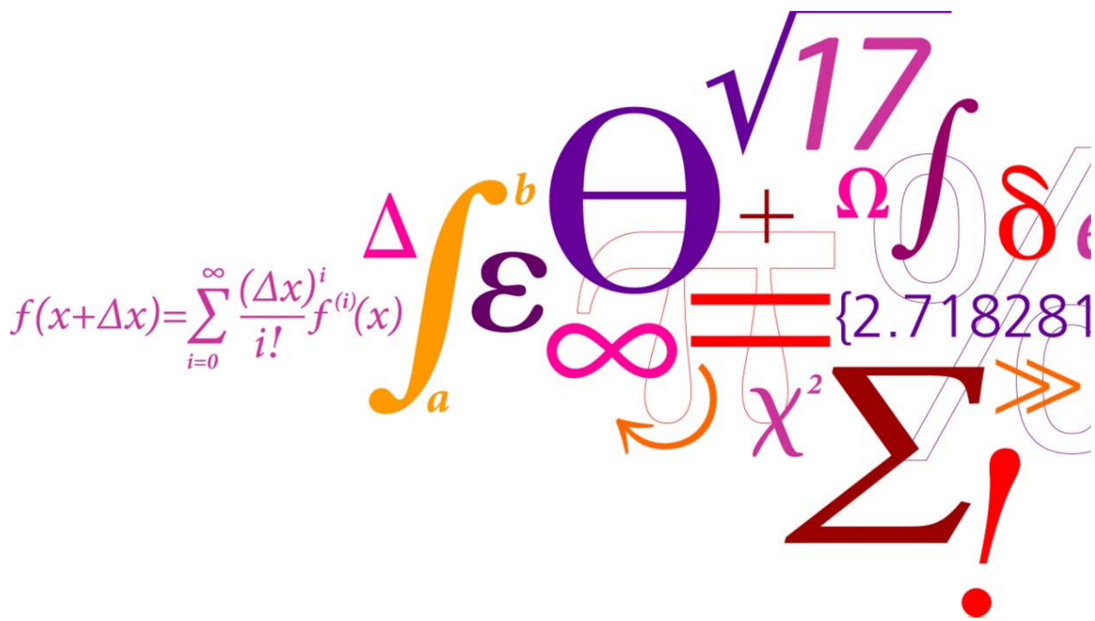
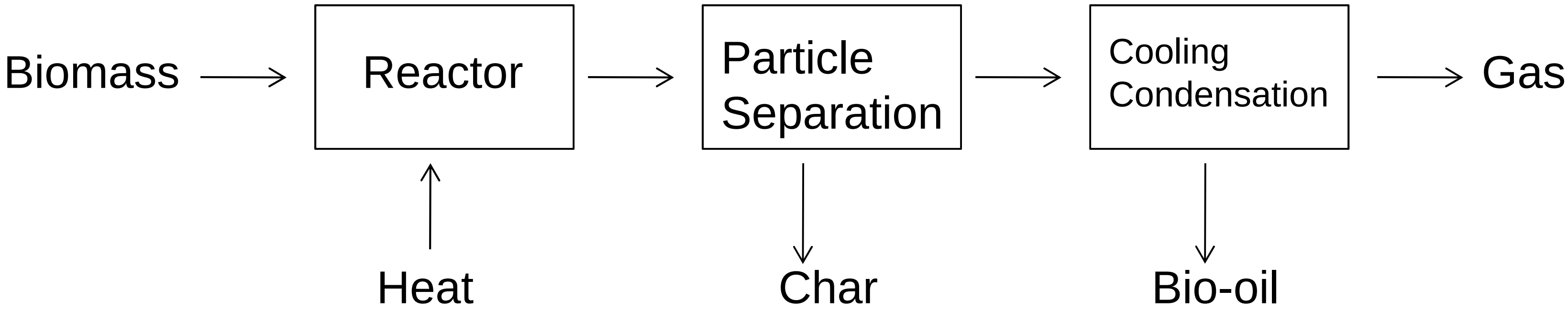
DTU, Chemical Engineering, CHEC



Flash pyrolysis process



Fast inert heating of biomass to produce a liquid product (bio-oil)
Also gas, water, and char is produced

<u>Typically operation values</u>

Heating rates:	> 300 k/s
Gas residence time:	< 2 s
Maximum temperatures:	450 – 600ºC
Feedstock types:	Wood, Straw …

Flash pyrolysis product – Typical bio oil properties

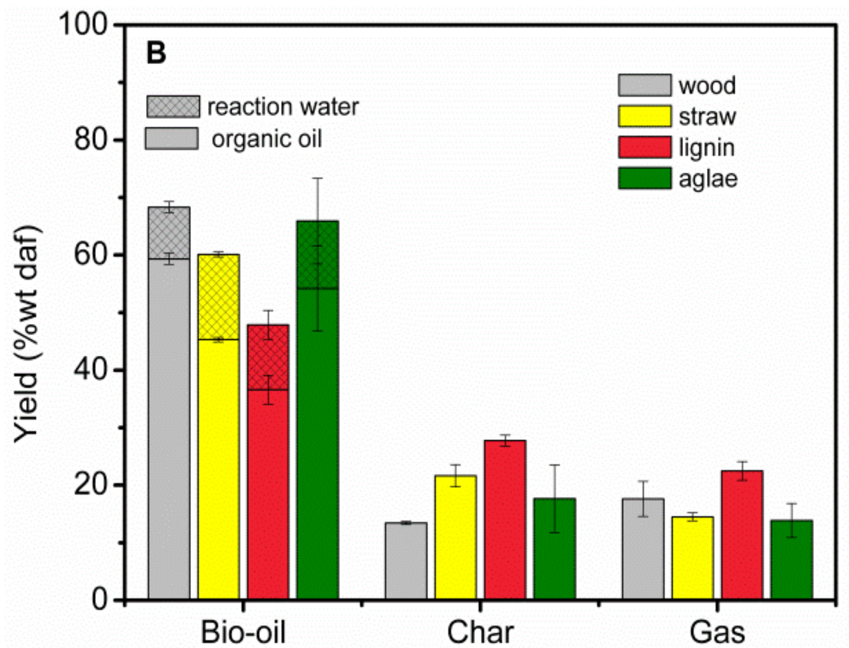
Bio-oil: Liquid organics plus water –(immiscible with fossil oil)

	Bio-oil	Heavy fuel oil
Water content:	15-30 wt%	0.1 wt%
(On dry basis)		
Heating value:	16-19 Mj/kg	42-44 Mj/kg
C content:	55-65 wt%	83-86 wt%
O content:	28-40 wt%	<1 wt%
H content:	5-7 wt%	11-14 wt%
Density:	1.2 kg/l	0.86 kg/l
Viscosity:	25 – 1000 cp	
PH	2 – 4	
Ash:	0,1-1 %wt	
Species:	- Oxygenated compounds 18 to 10,000 g/mol Acids, Alcohols, Sugars, Aldehydes, ketones, lignin residuals - Can be unstable when stored	

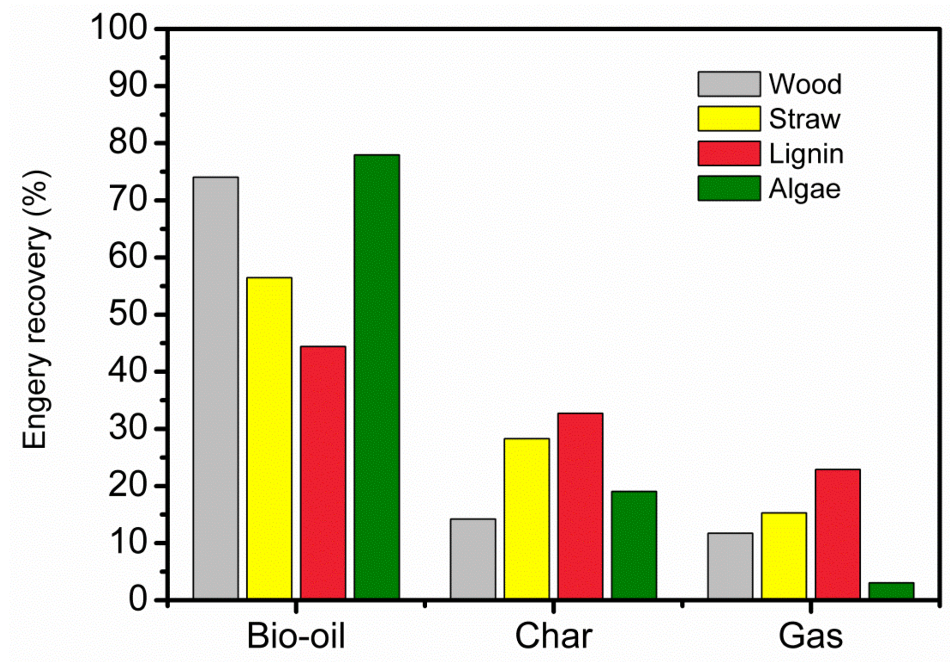
Reference: Venderbosch 2009, Review

Fast Pyrolysis bio-oil yields of different biomasses

Yields based on dry ash free basis



Energy Distribution



From reference: PhD work by Trung Ngoc Trinh, 2012.

Production of biomass based liquid fuels – comparison of different technologies

The production capacity (transportation fuel) per land area of different Bio-based technologies for liquid transportation fuels

	Land utilization [MJ/(m^2 y)]
Fischer-Tropsch	20.9-25.5
Second generation ethanol	18-25.2
HDO (H_2 from biomass)	30.1-35.0
HDO (H_2 from solar energy)	49.8

Reference. System study by: N. R. Singh, W. N. Delgass, F. H. Ribeiro, P. K. Agrawal, Environ. Sci. Technol. 44 (2010) 5298-5305.

Fast pyrolysis bio-oils:

Limitations: Relatively low quality oil

Advantages: high energy yield, simple technology

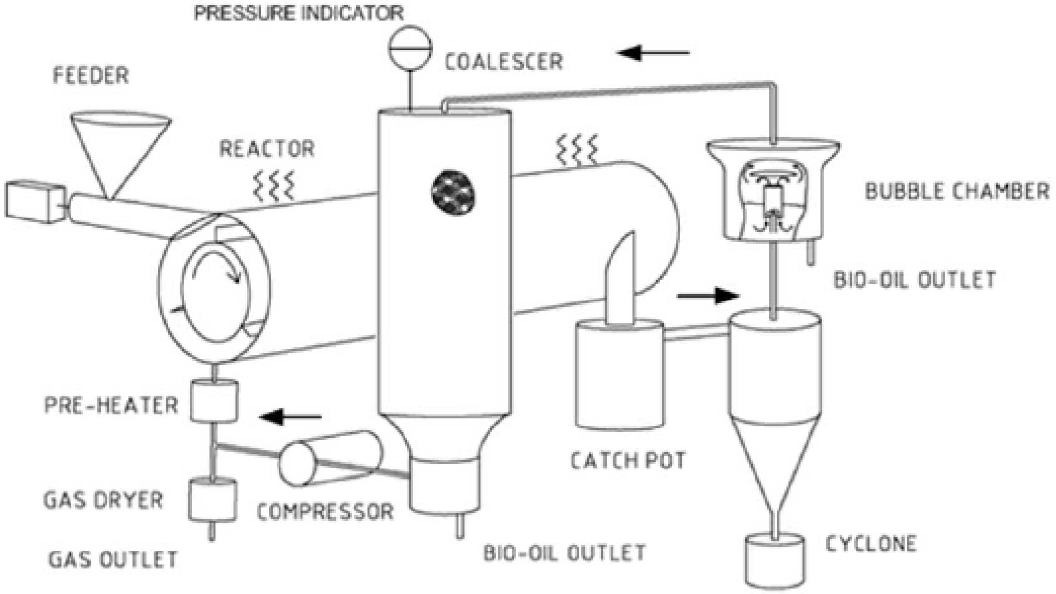
The use of fast pyrolysis bio-oil

Use as fuel in:	Limitations	Oil improvements
• Boilers	Stability, viscosity	Not needed Few boiler plant modifications
• Gas turbines	bio-oil ash	Filtering sufficient?
• Diesel engines (heavy)	Ignition delay, acidity	Emulsifications with biodiesel of fossil oil
• Diesel engines(light)	High viscosity, acidity, inhomogeneous, slow combustion.	Hydrodeoxygination (+ distillation)
• As a feed for oil refinery	Immiscible with fossil oil char formation when heated	Hydrodeoxygination

Fast pyrolysis process equipments – Ablative pyrolysis

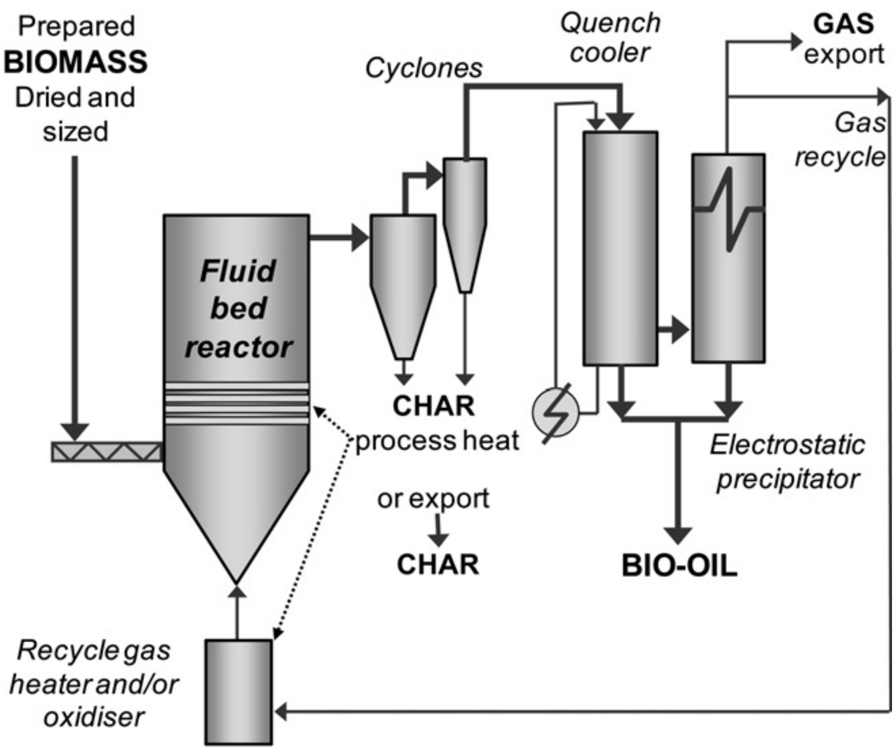
Pyrolysis of pine particle at high heating rate

DTU Pyrolysis Centrifuge Reactor PCR



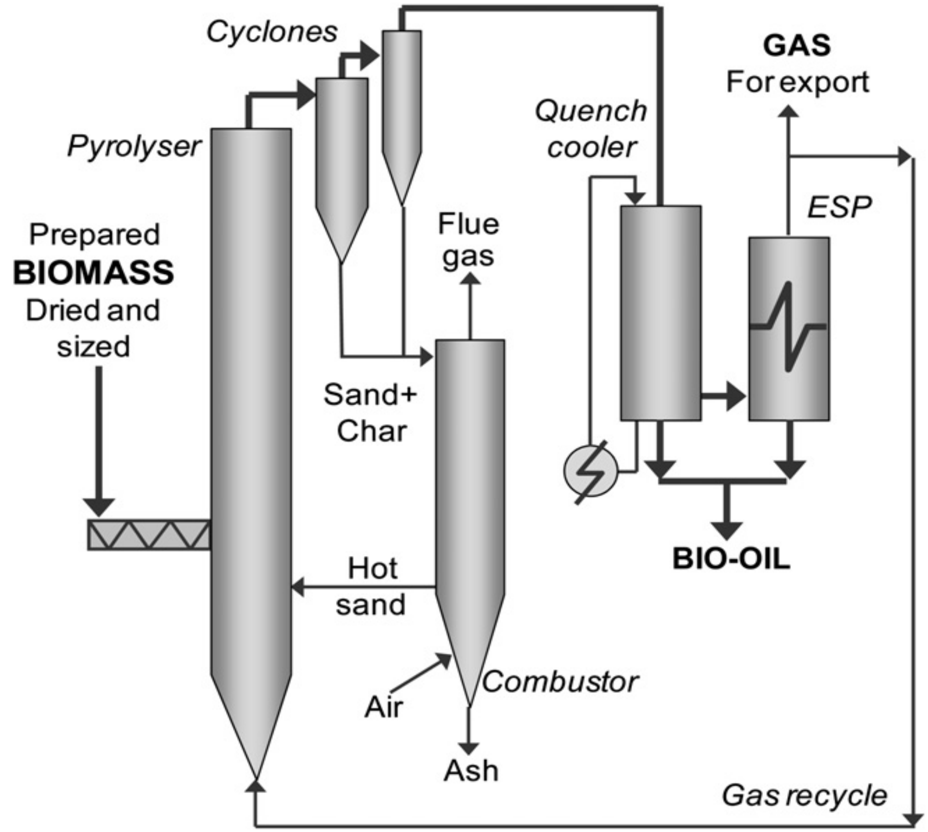
Fast pyrolysis process equipments – Fluid bed systems

Bubbling fluid bed reactor



Dynamotive type

Circulating fluid bed reactor

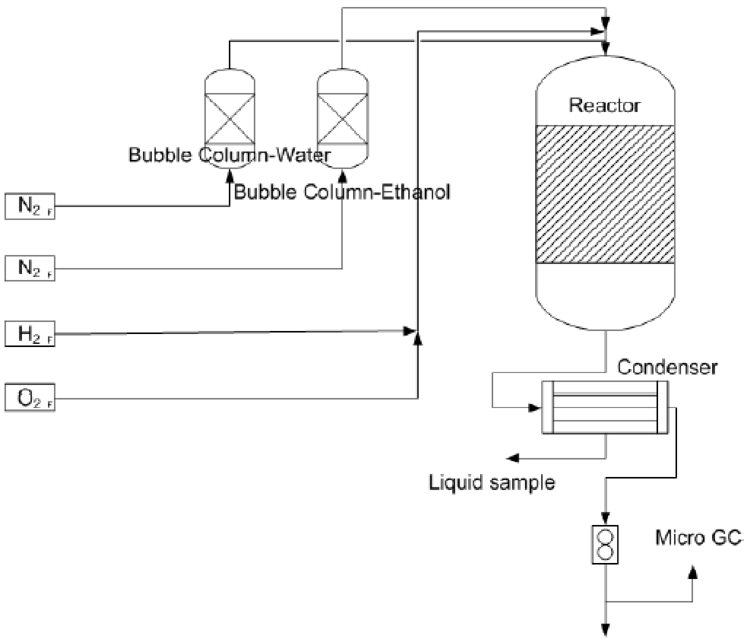


Ensyn type

From reference: Bridgewater A.V. Biomass and Bioenergy. **2012**.

Ongoing fast pyrolysis related research at DTU, Chemical Engineering

- Study on pyrolysis of different feedstock's on PCR and oil properties
- Studies on catalytic pyrolysis
- Up scaling of PCR



Study on catalysts for Steam reforming of pyrolysis oil

Study on catalysts for hydrodeoxygenation of pyrolysis oil – High pressure flow reactor, up to 125 bar and 550ºC

Global status of pilot/commercial biomass pyrolysis plants

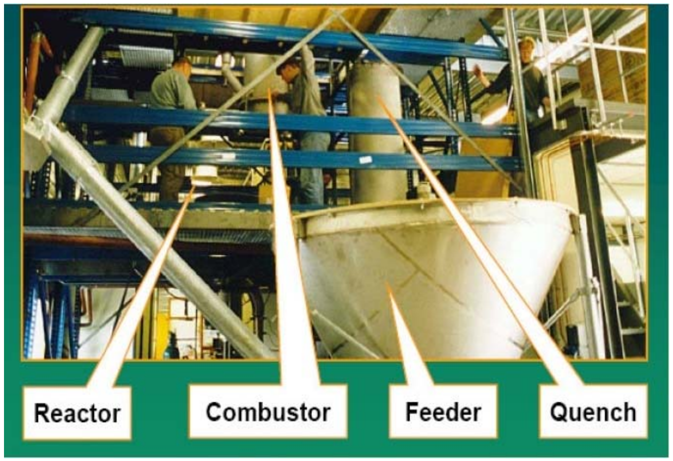
Some operating larger pyrolysis plants

Company	**Technol**	**Developments**
Dynamotive	BFB	Several plants, largest is 200tpd at west Lorne (CAN)
Ensyn	CFB	Several plants, largest is 100tpd plant in Renfrew (CAn); Construction of 9 plants in Malaysia by 2015 announced
BTG	RCR	120 tpd plant in Hengolo (NL) production of bio-oil, electricity, organic acids
B-O H N.V.	RCR	Largest plant is 12 tpd. Construction of two 5 tpd plants underway in NL and BEL
Biomass Eng.	BFB	4.8 tpd facility (UK)
KIT/Lurgi	Auger	12 tpd pilot plant in Karlsruhe (GER)

Circulating Fluidized Bed

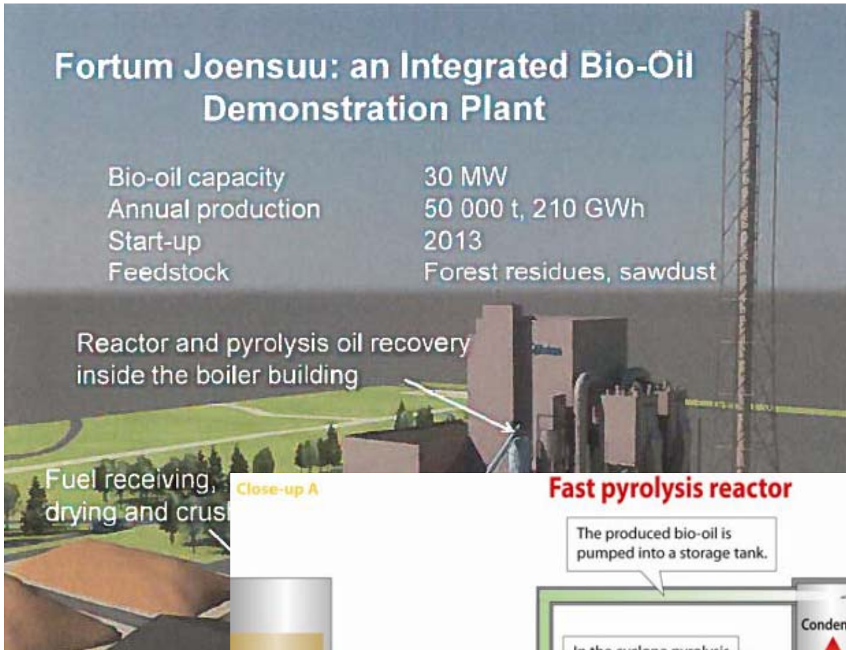
Ensyn(Canada):

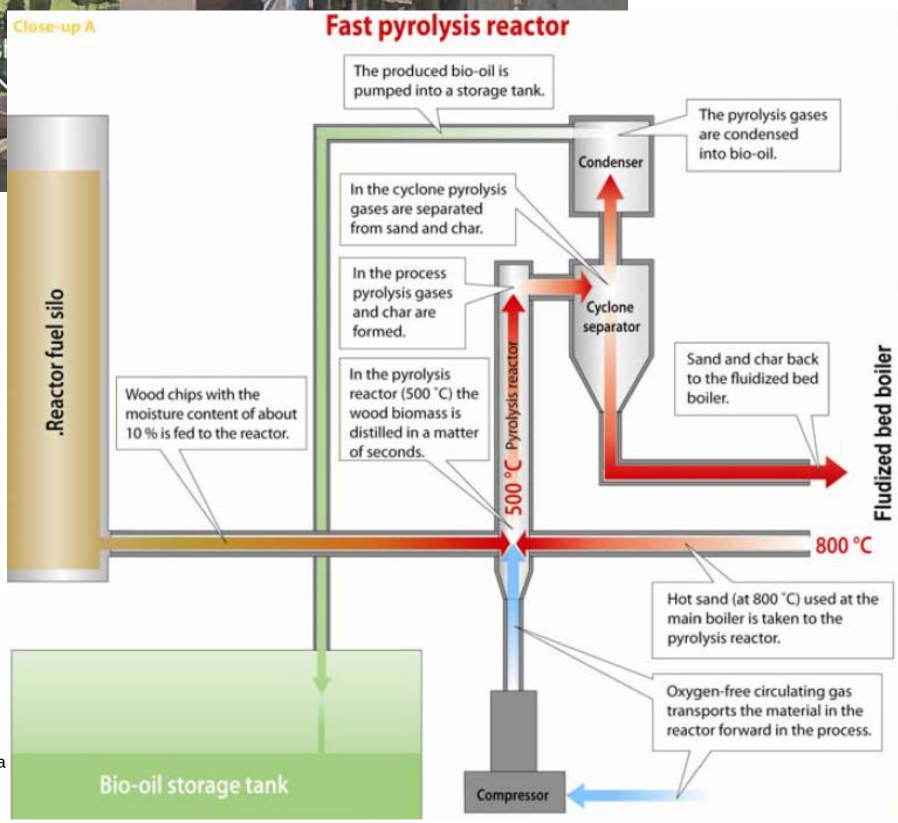
Rotating cone



BTG (NL)

Commercial biomass pyrolysis plants – Joensuu Finland

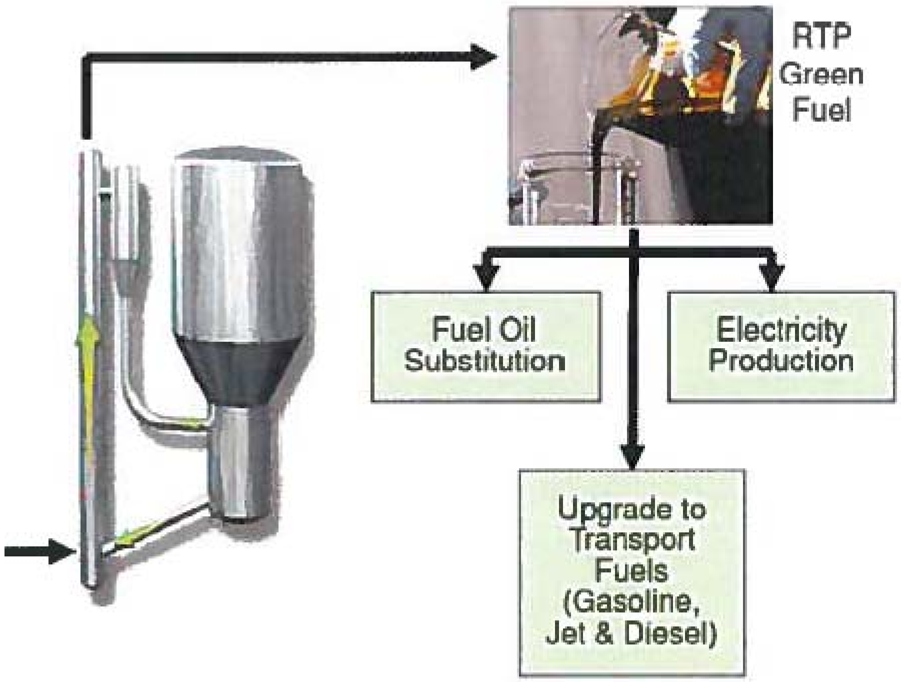




Company: FORTUM(FI)

- 170 t wood pd
- Two integrated fluid beds, combustion and pyrolysis,
- Reduce heavy fuel oil consumption
- First integrated plant with heat and electricity
- Start 2013
- Pyrolyser integrated fluid bed

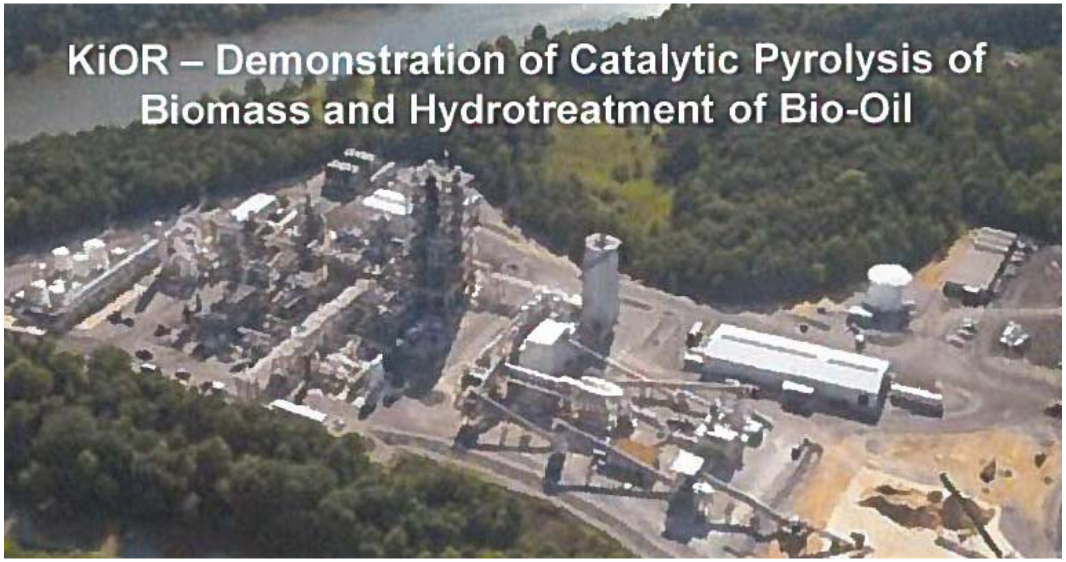
Commercial biomass pyrolysis plants – Evergent – Kapolei - Hawaii



Company: Envergent = Honeywell UOP + Ensyn Corp.

- pilot - 1 t biomass pd
- Integrated Pyrolysis and Catalytic Hydroconversion
- To produce transportation fuels
- Operations starts 2014
- Pyrolyser – Ensyn
- Financed by: US department of energy

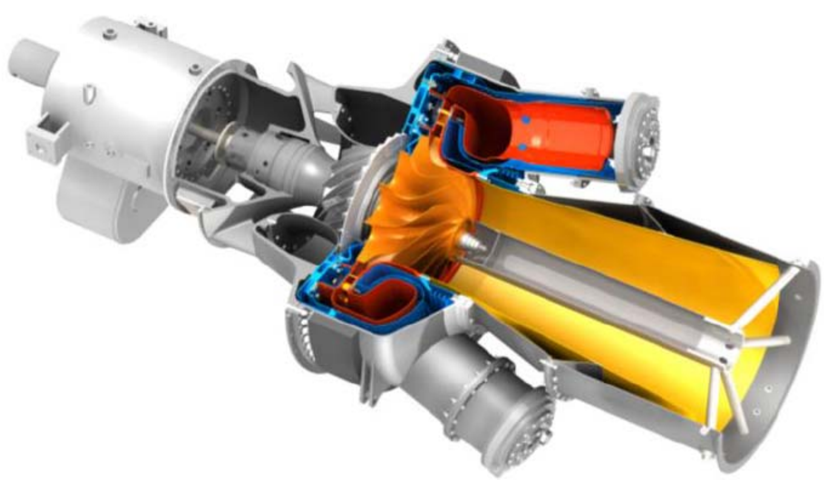
Commercial biomass pyrolysis plants – KiOR – Columbus US



Company: KiOR. (Taxas, US)

- 500 t biomass pd processed
- $213 mill
- Integrated Catalytic Pyrolysis and Catalytic Hydrotreatment
- To produce bio-crude to be processed in conventional refineries
- initial crude for diesel/gasoline produced in the start of 2013
- tech?

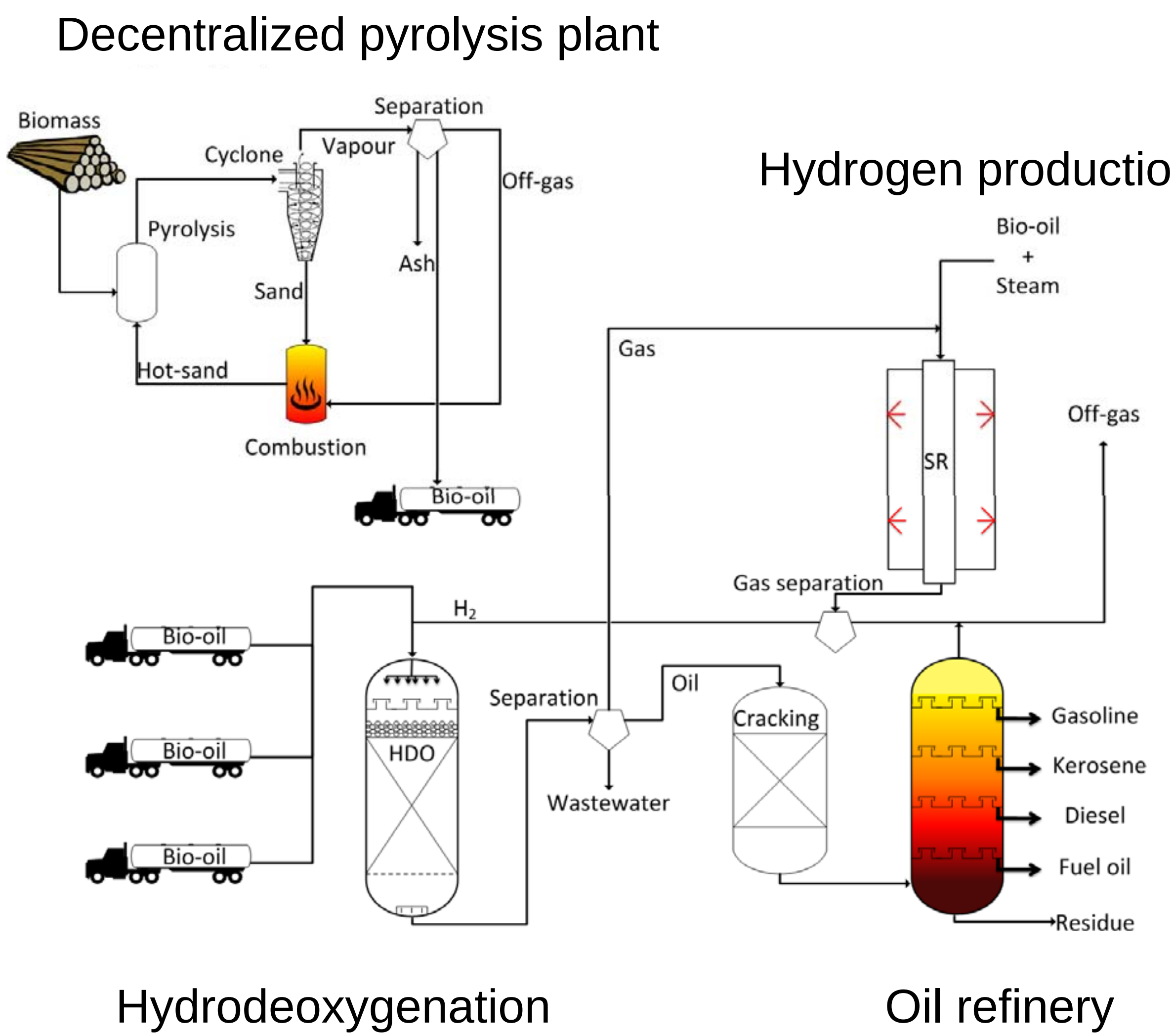
Commercial biomass pyrolysis plants – Tweente Netherlands



Company: BTG(NL).

• 200 t biomass pd
• Modified rotary cone pyrolysis reactor
• To produce electricity by use of gas turbine
• Operations starts 2014

Upgrading of fast Pyrolysis bio-oil



Upgrading of fast Pyrolysis bio-oil

Global ideal reaction HDO (hydrodeoxygenation):

$$CH_{1.43}O_{0.43} + 0.71H_2 \longrightarrow 1"CH_2" + 0.43H_2O$$

Exothermic production of gas, oil and water

- Reactor conditions: 80 – 200 bars, 300 – 400ºC
- Type of catalysts: $Co\text{-}MoS_2/Al_2O_2$, Pd/C, Ni/ZrO_2 ,$Ni\text{-}MoS_2$/…
- Limitations: - Coke formation and de activation by Cl, S, K
  - High hydrogen consumption

Zeolite cracking Global ideal reaction:

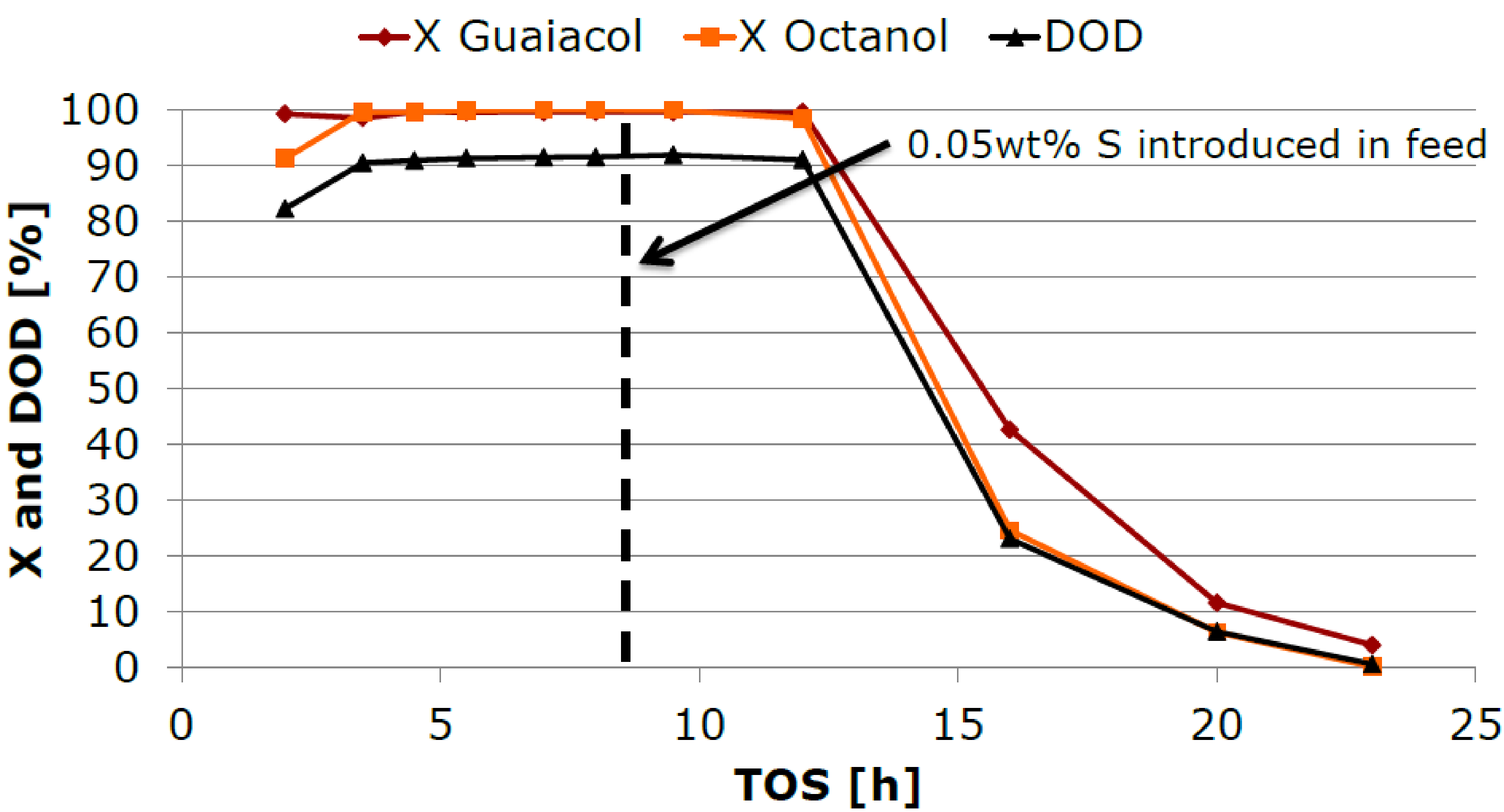
$$CH_{1.43}O_{0.43} \longrightarrow 0.88"CH_{1.2}" + 0.12CO_2 + 0.19H_2O$$

- Reactor conditions: 330 – 500ºC, 1 bar
- Limitations: - Low H/C content of product
  - Coke formation on the zeolite

Reference: Mortensen P. M. et Al. Applied Catalysis A. 2011, vol 407, 1-2, pp. 1-19.

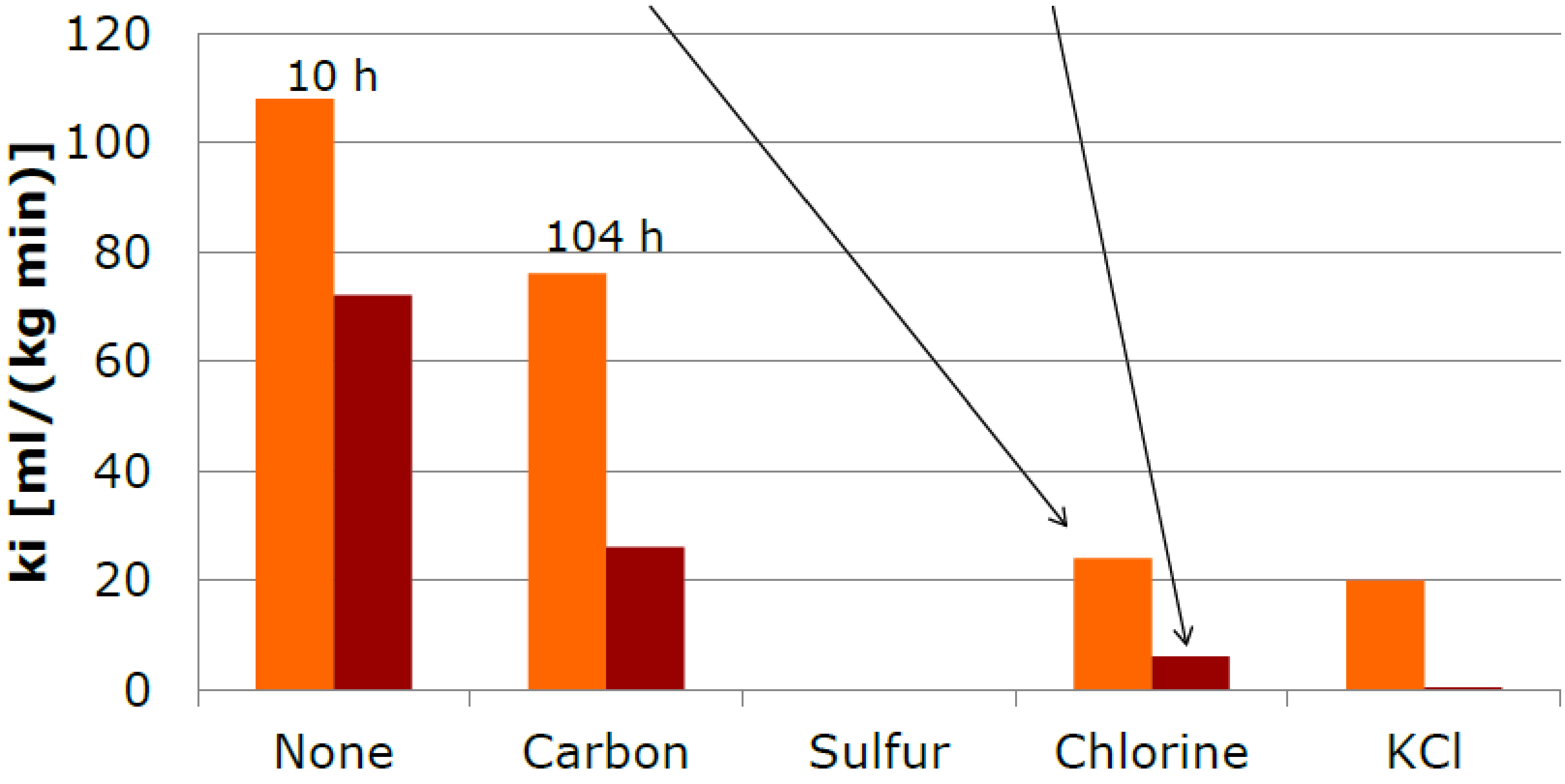
Upgrading of fast Pyrolysis bio-oil – deactivation of catalyst

Guaiacol hydrodeoxygenation at 100 bar and 250ºC
Sulfur deactivation of Ni/ZrO_2 catalyst



Upgrading of fast Pyrolysis bio-oil – deactivation of catalyst

Guaiacol hydrodeoxygenation on Ni/ZrO_2 catalyst
Deactivation by: Carbon formation/ S / Cl / K



Integrated catalytic hydropyrolysis and hydrodeoxygenation

Biomass → Pyrolysis Reactor → Separation → HDO → cooling → Gas

Cat + H_2 → Pyrolysis Reactor

Separation → Char

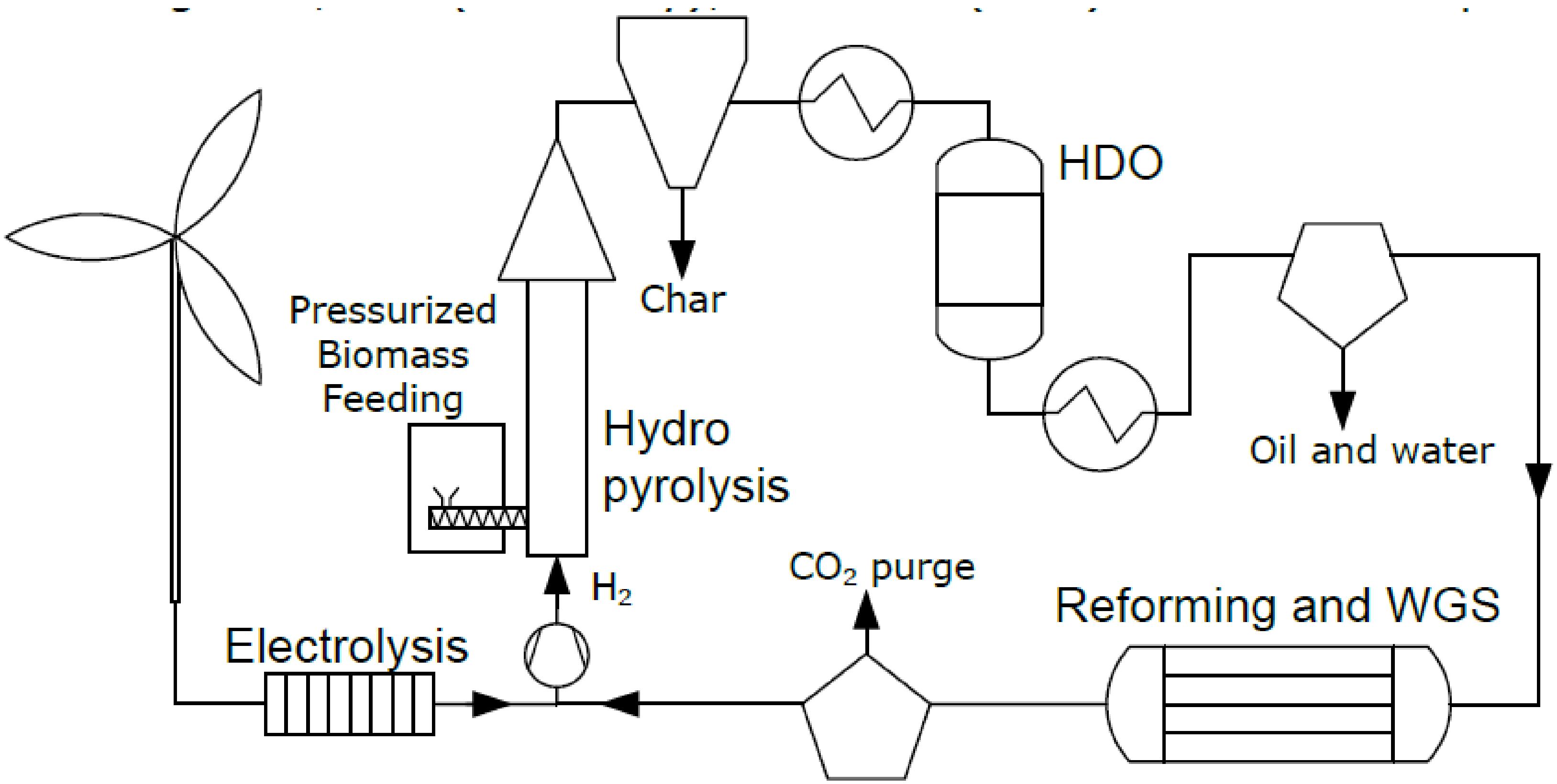
cooling → Oxygen free oil

Advantages:
- No re-heating of bio-oil is needed (prevent polymerization)
- Partial deoxygenation during pyrolysis

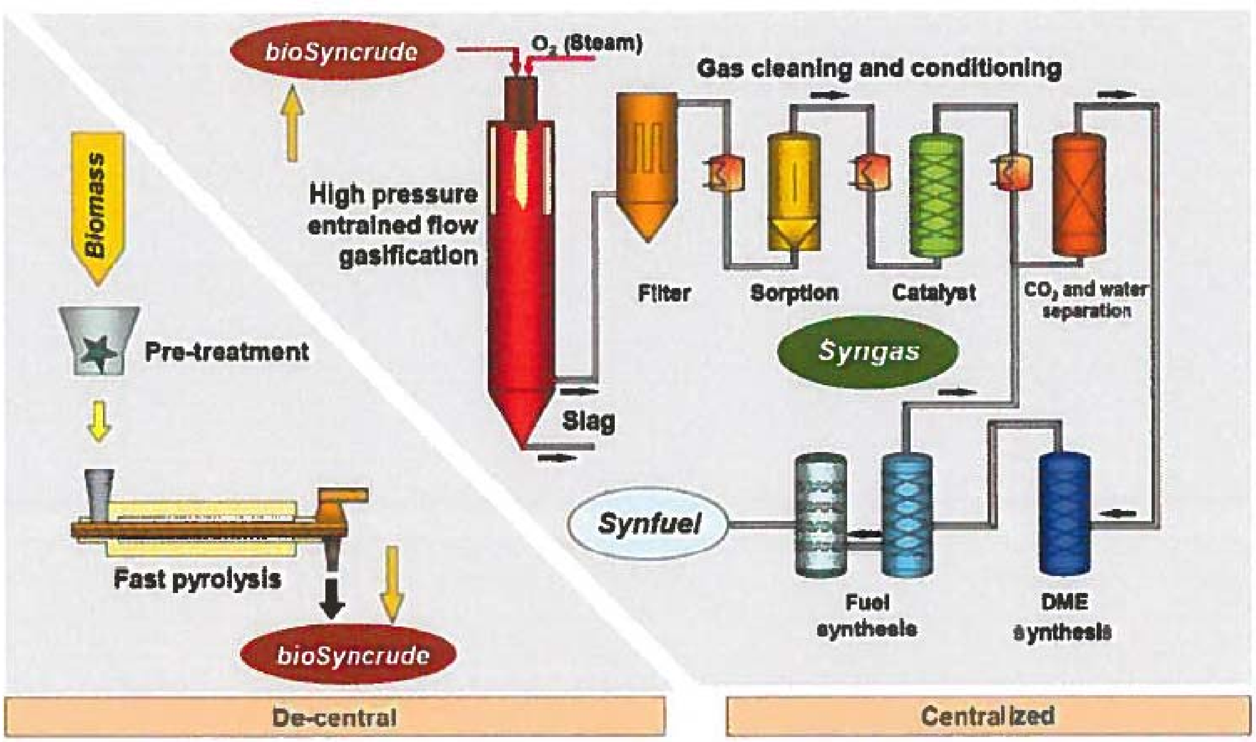
The GTI (IH^2) process:
- Temp: 350-480ºC/340-400ºC pressure 20 – 35 Bar.
- Yields: 20 -30 wt% (energy 55-80% Including a lot from H_2)
- Oxygen in product: < 1wt%
- Cat: ? De-activation and Cat stability ?
- Easy separation of water and oil

Gasoline-Range Hydrocarbons | Diesel/Jet-Range Hydrocarbons | Aqueous Product

Integrated catalytic pyrolysis



Alternative uses of the fast pyrolysis Technology – Oxygen blown pressurized gasification to produce liquid fuels

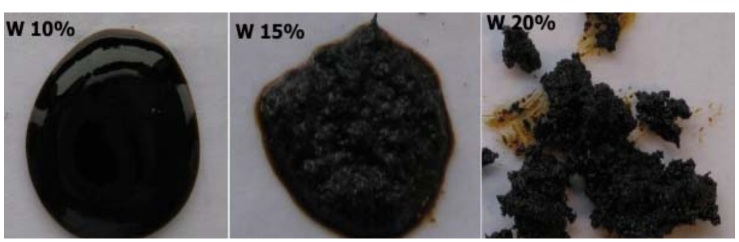


Research center Karlsruhe

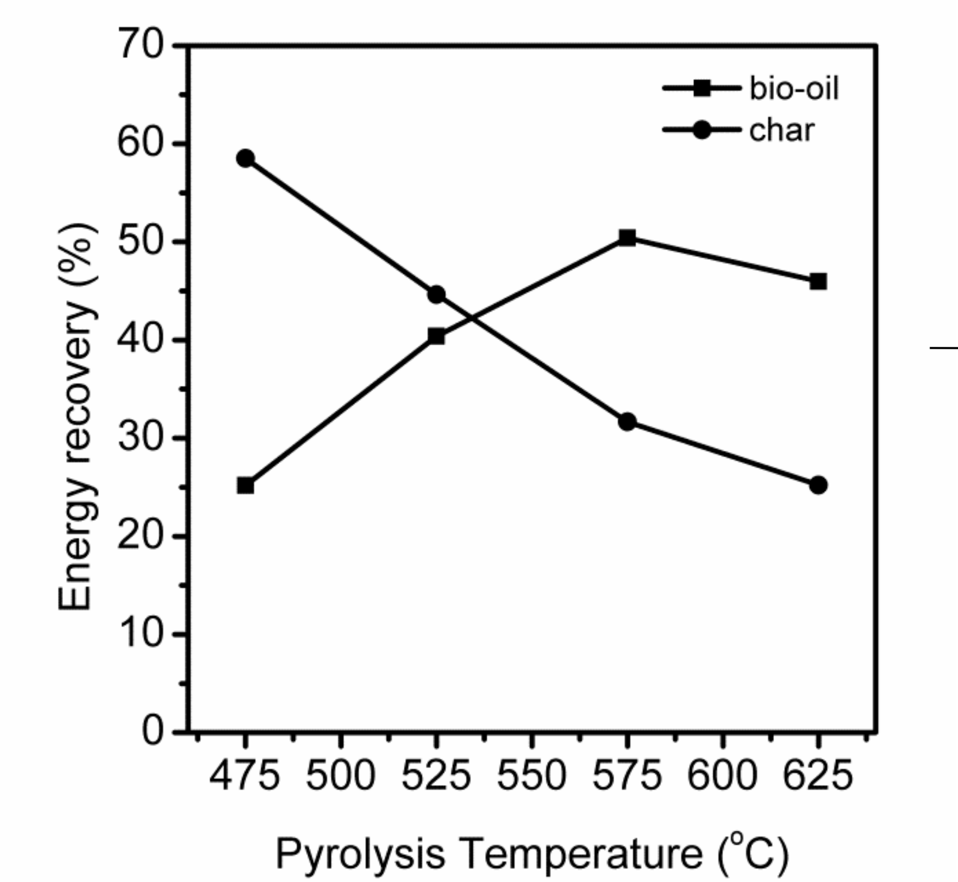
Decentralized pyrolysis followed by centralized gasification

Feeding of char and pyrolysis oil to gasifier

Char/bio oil Slurries



Alternative uses of the fast pyrolysis Technology - Pyrolysis treatment of sewage sludge



Pyrolysis Reactor

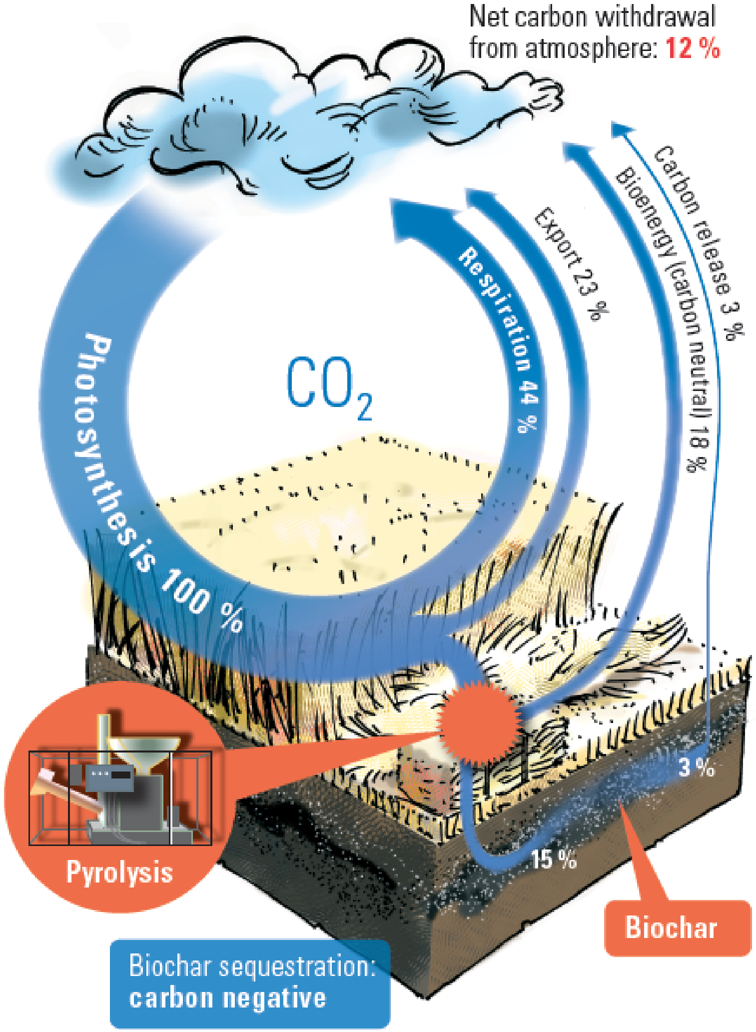
<u>Oil:</u>
- Most of heating value

<u>Char:</u>
- Containing P, K ..
- Reduced volume to disposal

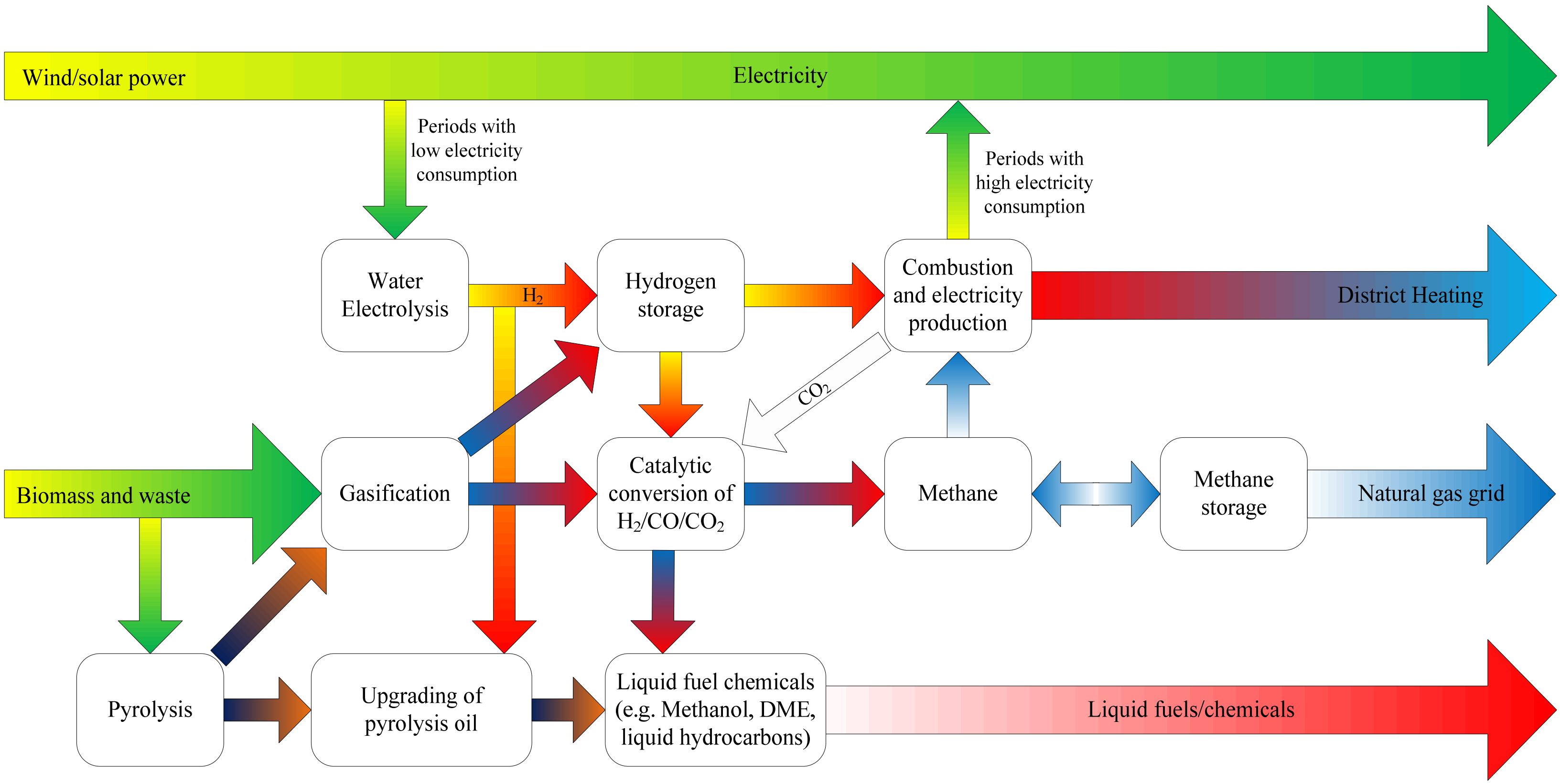
Alternative uses of the fast pyrolysis Technology
Pyrolysis on the field combined with bio-char

Concept of in-situ treatment

Bio-Char carbon sequestration



Integration of renewable electricity production and production of liquid fuels



Perspectives

- A lot of research and commercial activities globally
- Difficult to asses the status of commercial activities
- Is pyrolysis the future biomass transport fuels technology?: - limit plant complexity – cheap catalyst that: – not deactivates – have a high yield – limited H_2 consumption.
- Limited upgrading and use as ship engine fuels
- Pyrolysis as a process step in biomass treatment plants:
  - Pressurized gasification feeding of slurries
  - Sludge treatment
  - Lignin from ethanol plant treatment
- Possibly a on fields in-situ technology